

Pattern Fitting for Quantitative X-Ray Powder Diffraction Analysis of Portland Cement and Clinker ¹

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Abstract

X-ray powder diffraction is a direct method for qualitative and quantitative phase abundance analysis of fine-grained, crystalline materials. While the application of powder diffraction for qualitative analysis in the cement industry is well established, its use in the determination of phase abundance is not as common. Difficulty in measurement of peak intensity and availability of suitable reference standards have limited the application of X-ray diffraction in quantitative analysis. Whole-pattern fitting offers a means to address these problems by using all diffraction peaks to estimate individual phase pattern intensities. Dataplot, a graphics and data analysis language, facilitates pattern-fitting and quantitative phase abundance analyses by applying multivariate linear least-squares regression based upon experimentally derived X-ray diffraction reference patterns. Phase abundance calculation by the internal standard method uses the pattern scale factors calculated in the fit as intensity values. Precision of replicate analyses by pattern fitting show a distinct improvement over measurement by peak profile fitting. Trials using known mixtures of clinker interstitial phases indicate a very good agreement with the known phase abundance values, and absolute errors, based on the whole cement, of less than 1 percent.

Keywords

clinker, phase composition, portland cement, quantitative analysis, qualitative analysis, whole-pattern fitting, X-ray powder diffraction

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Introduction

Classification of cements as Type I through Type V, in part, reflects the influence of phase composition on cement and concrete performance. The ability to accurately determine cement phase composition should lead to a better understanding of the effects of composition on performance of cement and concrete.

Methods employed in phase composition analysis include microscopy, chemical analysis, and X-ray powder diffraction. Microscopical methods provide direct analysis suitable for clinker, but due to their fine particle size, are rarely applied to ground cements. The fine crystal size of some phases often make their identification and quantitative determination by microscopy a difficult, time-consuming task. Chemical data are also used to determine the potential phase composition via the Bogue calculation. This is an indirect method, and the potential compositions are often in significant error as compositions of the actual clinker phases are not those assumed in the calculation [1].

X-ray powder diffraction (XRD) is a direct method for qualitative and quantitative characterization of fine-grained materials such as clinker and cement, and may also be used for analysis of raw materials. Each phase produces a unique diffraction pattern independent of others, with the intensity of each pattern proportional to that phase's concentration in a mixture.

However, clinker and cement phase powder diffraction patterns are complex, and the large number of phases creates a composite pattern with many peak overlaps. Compositional and structural variations of each phase influence peak positions and its relative intensity. Difficulties common to many diffraction studies of cement [2-9] include peak intensity measurement and the selection of appropriate reference standards. Most of these efforts relied on intensity measurements of single, resolvable diffraction peaks; for cements, however, these peaks are very weak and therefore difficult to measure.

An alternate technique may be found in whole-pattern fitting. Whole-pattern analysis in quantitative powder diffraction of cements has its origins in the efforts of R.L. Berger et al. [5] in 1964. Use of the entire pattern allows all diffraction peaks to be used in estimation of the pattern intensity. Reference pattern suitability may be evaluated by the quality of fit: graphically through the residual error plot; numerically by the residual standard deviation; and to assess the significance of a parameter in the fit, the t-value. The pattern weights serve as intensities and mass fractions are calculated using an internal standard analysis. Adaptations of this procedure have been implemented by others [4,6-7], and in the 1980's, methods employing the entire diffraction pattern have been seeing a resurgence in popularity.

A measured diffraction pattern of a multi-phase material may be considered a dependent variable, and each $2-\theta$ step an independent observation. The intensity for each observation is a linear combination of the diffraction patterns of each phase plus the background. Multivariate linear regression by the method of least-squares incorporates all observations along the diffraction trace to establish the "best-fit" set weights by minimizing sum of squares of the deviations between the observed and calculated patterns.

Whole-pattern fitting using a set of reference patterns differs from the Rietveld method [10], in which reference patterns are calculated by refinement of the crystal structure, instrumental, and specimen characteristics. The reference pattern approach assumes that the reference phases are representative of those in the mixture; therefore a reference pattern database including expected polymorphs for each phase is necessary. Gutteridge [7] selected the reference set producing the lowest residual error.

Pure clinker phase standards are commercially available, may be synthesized in the laboratory, or for some phases, separated from the clinker by selective extraction methods. The ICDD database [11] often provides a description of procedures for synthesis of the phases. Alternative methods include extraction of a diffraction profile from a composite pattern, synthesis from a d-spacing and relative intensity file, and calculation of a diffraction pattern from structural and chemical data.

Graphics and Analysis

Dataplot [12], a graphics and data analysis language developed at NIST, is being used by the author for whole-pattern fitting analysis. Dataplot was designed to address data analysis problems, is interactive, and uses descriptive, English-syntax commands (see Appendix A). Macro files for tasks such as reading reference data sets, fitting, and calculation of calibrations and mass fractions may be written to automate the analyses.

First, a database of diffraction patterns from both pure phases and multi-phase mixtures of known phase proportion that include an internal standard must be collected. Each pattern is corrected for zero-error, then a background curve is fit and subtracted, and each pattern is normalized to 1000 counts to place them on a similar scale. The calibration establishes the relationship between the pattern intensity ratio and mass fraction ratio of each phase and an internal standard. The pattern intensity in a mixture, calculated using Dataplot, is a measure of each phase's intensity relative to its reference pattern. This output is in the form of pattern weight estimates, their standard deviations, and a t-value, which may be used to assess the significance of that variable in the fit (Figure 1). The residuals are the difference between the observed and calculated patterns, so the residual standard deviation reflects the quality of the fit.

Figure 1. Output from least squares fit giving weight factors, standard deviations, t-values, and residual standard deviation for unknown mixture 1, replicate 1.

LEAST SQUARES MULTILINEAR FIT

SAMPLE SIZE N = 2250
 NUMBER OF VARIABLES = 5

| | PARAMETER ESTIMATES | | | (APPROX. ST. DEV.) | T VALUE |
|---|---------------------|---------|--------------|--------------------|----------|
| 1 | A0 | | 1.39365 | (0.2840) | 4.9 |
| 2 | A1 | C3A-CUB | 0.490770 | (0.6064E-02) | 81. |
| 3 | A2 | C3A-ORT | 0.365170E-01 | (0.4458E-02) | 8.2 |
| 4 | A3 | C4AF | 0.984071 | (0.3476E-02) | 0.28E+03 |
| 5 | A4 | MGO | 0.449247 | (0.2900E-02) | 0.15E+03 |
| 6 | A5 | TIO2 | 0.366017 | (0.3227E-02) | 0.11E+03 |

RESIDUAL STANDARD DEVIATION = 11.572788

The diffraction plots of the raw data (including background), calculated patterns, and residual plot are presented in Figure 2. The calculated pattern is the sum of each reference pattern multiplied by it's weight estimate. The plots presented here include the individual phase calculated patterns that are background-subtracted. A plot of the residual values, raw data, and calculated patterns against the two-theta scale allows visual examination of the quality of the fit. Problems such as mis-alignment of any patterns, phases present but not included in the fit, and poor reference selection all are apparent in the residual profile.

In this example, deviations in the residual plot reflect sample displacement that is smaller than a single $2-\theta$ step, and some differences in the ferrite peak positions. While a sample displacement pattern shift will influence the calculated pattern weights, minor shifting of some peak positions appears to be less of an influence on pattern intensity weights. Taylor [13] suggests integrating larger $2-\theta$ regions to lessen the influence of peak shifting. Experiments merging these diffraction patterns to 0.25° and 1° $2-\theta$ intervals have been successful, but have not yet been applied to industrial clinkers.

The Internal Standard Method for Quantitative Analysis

While intensity is proportional to phase concentration, this relationship is usually not linear, due to absorption of the X-ray beam by the mixture. Klug and Alexander [14] demonstrated that in a multi-component mixture, an internal standard added to the sample in a known proportion could be used to correct for absorption effects. Calibrations are determined for each phase by preparing mixtures of known phase proportions, including a known proportion of internal standard, determining the pattern intensities for a set of calibration, and calculation of the reference intensity ratio (RIR).

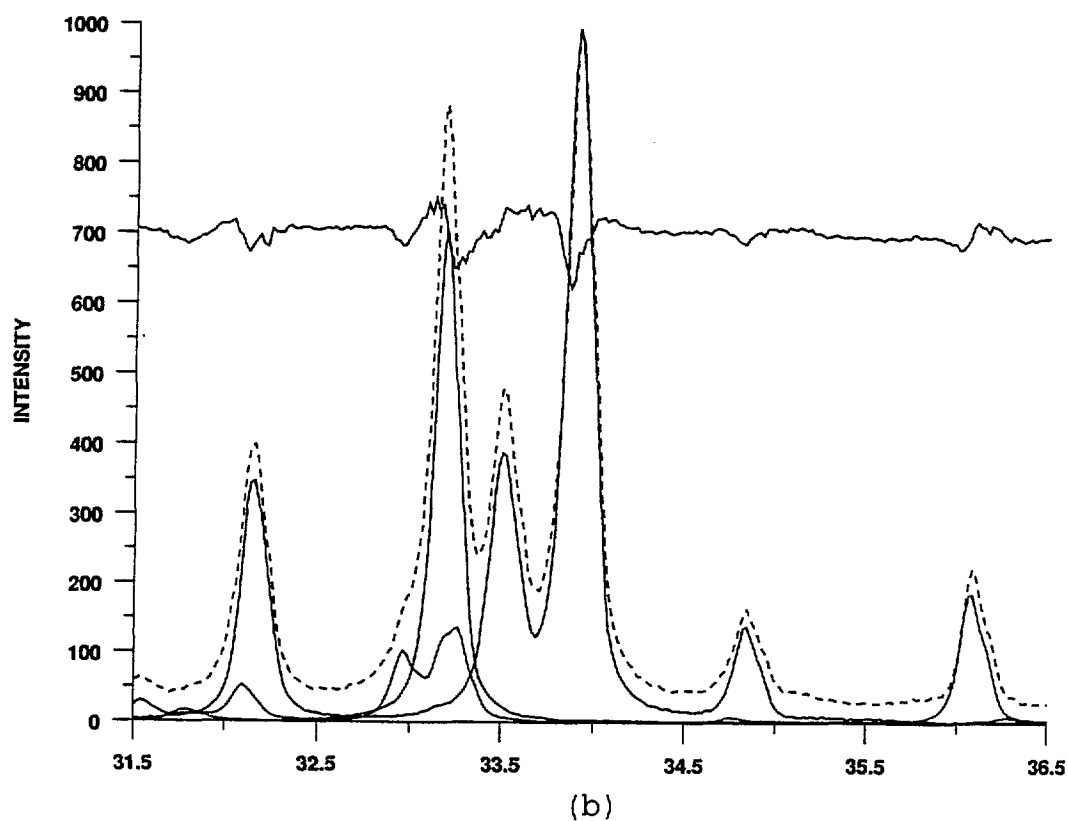
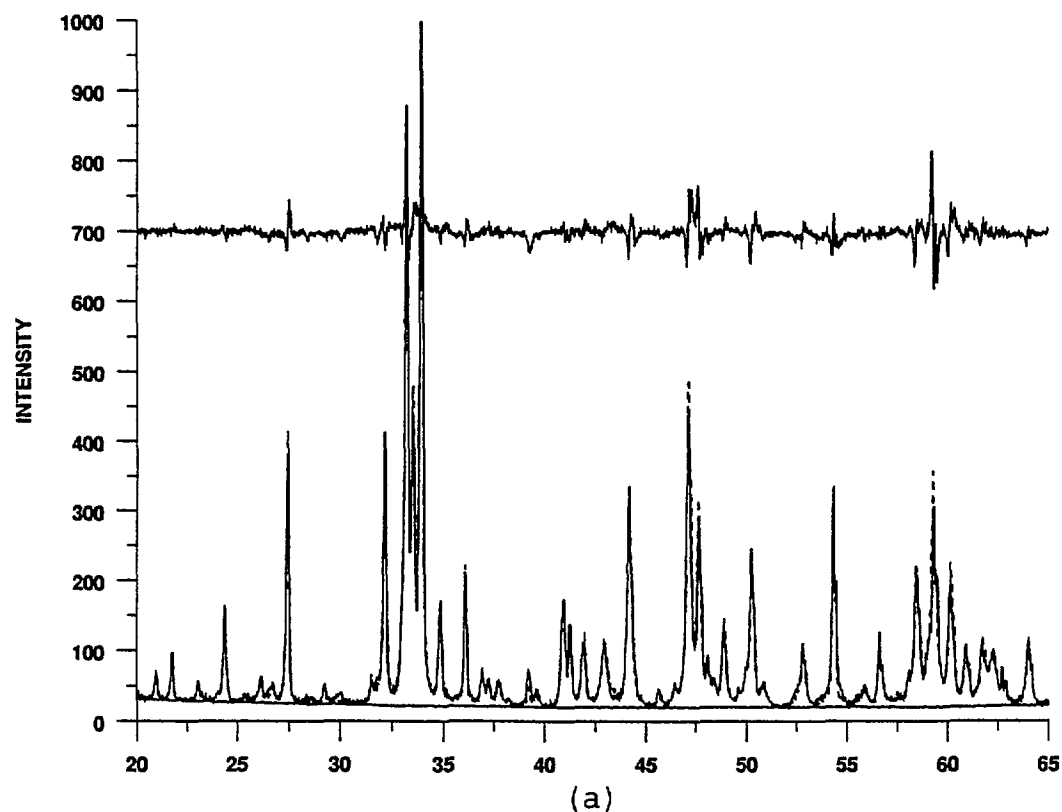


Figure 2. Diffraction plot (a) showing raw data, predicted pattern, residual plot (centered around $I=700$), and an expanded plot (b) showing the raw data (dashed) and calculated patterns, based on the least-squares fit, for cubic and orthorhombic aluminate, ferrite, and rutile.

The Reference Intensity Ratio Technique

The reference intensity ratio technique [15] is an adaptation of the internal standard method where the slope, RIR, of the calibration plot is given by:

$$\frac{I_{\alpha}}{I_s} \times \frac{X_s}{X_{\alpha}} = RIR_{\alpha} \quad (2)$$

where:

- I_s = pattern intensity of internal standard s,
- I_{α} = pattern intensity of phase α ,
- X_{α} = mass fraction of phase α , and
- X_s = mass fraction of internal standard s,

Calibration using the RIR method requires three steps:

- a) collection of diffraction patterns of individual phases for reference profiles;
- b) collection of diffraction patterns of multi-phase mixtures of known composition with a known mass of intermixed internal standard; and
- c) calculation of pattern intensities and of the RIR constant relating peak intensity ratio with mass fraction ratio using eq. (2).

Analysis of the unknown mixture involves the following:

- a) addition and homogenization of a known mass of internal standard;
- b) three replicate diffraction scans, repacking for each;
- c) measurement of background-subtracted intensities; and
- d) calculation of the mass fraction of each phase using eq. (3):

$$\frac{I_{\alpha}}{I_s} \times \frac{X_s}{RIR_{\alpha,s}} = X_{\alpha} \quad (3)$$

Mass fractions of the unknown are of a mixture including the internal standard. Correct for the internal standard using eq. (4):

$$X'_{\alpha} = \frac{X_{\alpha}}{1 - X_s} \quad (4)$$

Calibration and Analysis

This data set is from the NIST contribution to the cooperative calibration initiated by the ASTM C01.23.01 task group on X-ray powder diffraction. This effort is part of an effort to develop a test method for quantitative analysis of clinker and cement phase abundance [8]. Three calibration and two unknown mixtures were prepared by blending a 12% internal standard addition and homogenized by mortar and pestle. Three replicate powder mounts were prepared for each mixture. Intensity data, calibration constants, and mass fraction estimates were calculated as discussed earlier (Table 1).

Summary and Conclusions

Table 2 presents the results of analysis of two test mixtures using both the whole-pattern fitting approach and the older method of profile-fitting individual diffraction peaks. The test mixture true values reflect the desired phase abundance compositions and were prepared by proportioning pure phases, by mass, using an analytical balance. Both methods provide similar results compared to the true values however, the pattern-fitting data exhibit much better precision as indicated by the standard deviations and 95% confidence intervals. Some bias is present as some of the calculated mass fractions fall outside the standard deviation reproducibility range. The identification of orthorhombic aluminate in unknown sample 1, where none was present, is the result of a RIR value skewed by an outlier RIR from calibration mixture 2. Additional calibration points for all phases should improve the data and lessen the influence of any outlying RIRs.

These test mixtures reflect the interstitial phases in a clinker containing 17%, by mass interstitial compounds. Their mass fraction values re-calculated on the basis of a bulk cement are good showing absolute errors below 1 percent.

Compositional and structural variations found in industrial clinkers may result in lower accuracy unless comparable phases for reference standards can be obtained. This is not unreasonable, as selective extractions allow concentration of individual phases or groups of phases. Alternatively, diffraction profiles may be extracted from the composite diffraction pattern or calculated based on chemical and structure data.

Table 1. Dataset for Quantitative X-ray Powder Diffraction Calibration for Interstitial Phases.

Known Mixture 1

| Phase | Mass | Pattern Intensity | | Scan 3 | Average I/I TiO ₂ | Std. Dev. |
|------------------------|------|-------------------|----------|----------|---------------------------------|-----------|
| | | Scan 1 | Scan 2 | | | |
| C ₃ A-Cubic | 65 | 0.985860 | 0.984324 | 0.980169 | 4.721346 | 0.0153 |
| C ₄ AF | 35 | 0.354054 | 0.351141 | 0.357382 | 1.700396 | 0.0136 |
| Rutile (IS) | 12 | 0.208758 | 0.207836 | 0.208304 | | |

Known Mixture 2

| Phase | Mass | Pattern Intensity | | Scan 3 | Average I/I TiO ₂ | Std. Dev. |
|------------------------|------|-------------------|----------|----------|---------------------------------|-----------|
| | | Scan 1 | Scan 2 | | | |
| C ₃ A-Cubic | 11 | 0.340935 | 0.350029 | 0.350460 | 0.868675 | 0.0065 |
| C ₃ A-Ort. | 51 | 0.700826 | 0.696038 | 0.699160 | 1.748516 | 0.0199 |
| C ₄ AF | 11 | 0.217044 | 0.219552 | 0.216170 | 0.544539 | 0.0070 |
| MgO | 27 | 0.644960 | 0.641183 | 0.64323 | 1.609496 | 0.0181 |
| Rutile (IS) | 12 | 0.395649 | 0.400211 | 0.402965 | | |

Known Mixture 3

| Phase | Mass | Pattern Intensity | | Scan 3 | Average I/I TiO ₂ | Std. Dev. |
|------------------------|------|-------------------|----------|----------|---------------------------------|-----------|
| | | Scan 1 | Scan 2 | | | |
| C ₃ A-Cubic | 29 | 0.692944 | 0.680578 | 0.690178 | 1.913957 | 0.0071 |
| C ₃ A-Ort. | 7 | 0.145421 | 0.138934 | 0.133077 | 0.387138 | 0.0166 |
| C ₄ AF | 60 | 1.011120 | 0.998785 | 1.003280 | 2.794588 | 0.0070 |
| MgO | 4 | 0.087225 | 0.084298 | 0.083400 | 0.236423 | 0.0050 |
| Rutile (IS) | 12 | 0.361090 | 0.357104 | 0.360028 | | |

Summary

| C ₃ A-Cubic | | C ₃ A-Ort. | | C ₄ AF | | MgO | |
|------------------------|----------|-----------------------|----------|-------------------|----------|------|----------|
| Mass | RIR | Mass | RIR | Mass | RIR | Mass | RIR |
| 11 | 0.947650 | 7 | 0.663667 | 11 | 0.594045 | 4 | 0.709274 |
| 29 | 0.791982 | 51 | 0.411416 | 35 | 0.582994 | 27 | 0.715334 |
| 65 | 0.871634 | | | 60 | 0.558919 | | |
| Avg. | 0.870422 | | 0.537542 | | 0.578653 | | 0.712304 |

Table 2. Quantitative X-Ray Powder Diffraction Data Expressed as Mass Percent Using Intensity Measurements by Whole-Pattern Fitting and Profile Fitting.

| Mixture 1 ² | Whole Pattern Fitting | | | | Profile-Fitting ³ | | | |
|----------------------------------|-----------------------|------------------|--------------------|-------------------------|------------------------------|--------------------|-------------------------|--|
| | True Value | Calculated Value | Standard Deviation | 95% Confidence Interval | Calculated Value | Standard Deviation | 95% Confidence Interval | |
| C ₃ A-Cubic | 20.0 | 18.6 | 0.1 | ± 0.3 | 20.7 | 1.0 | ± 2.4 | |
| C ₃ A-Ort. | 0.0 | 3.3 | 0.9 | ± 2.1 | 3.5 | 4.5 | ± 11.2 | |
| C ₄ AF | 58.0 | 57.8 | 1.6 | ± 3.9 | 55.9 | 4.2 | ± 10.3 | |
| MgO | 22.0 | 21.6 | 0.5 | ± 1.1 | 20.9 | 0.3 | ± 0.7 | |
| Mixture 2 | Whole Pattern Fitting | | | | Profile-Fitting | | | |
| | True Value | Calculated Value | Standard Deviation | 95% Confidence Interval | Calculated Value | Standard Deviation | 95% Confidence Interval | |
| C ₃ A-Cubic | 63.0 | 63.8 | 1.5 | ± 2.2 | 64.7 | 0.6 | ± 1.5 | |
| C ₃ A-Ort. | 7.0 | 8.6 | 0.6 | ± 2.3 | 10.1 | 4.0 | ± 9.8 | |
| C ₄ AF | 26.0 | 26.7 | 0.6 | ± 1.8 | 24.9 | 3.1 | ± 7.7 | |
| MgO | 4.0 | 4.2 | 0.1 | ± 0.4 | 0.8 | 0.2 | ± 0.4 | |
| Mass Fraction, Bulk Cement Basis | | | | | | | | |
| | Mixture 1 | | | Mixture 2 | | | | |
| | True Value | Calculated Value | Absolute Error | True Value | Calculated Value | Absolute Error | | |
| C ₃ A-Cubic | 3.4 | 3.2 | 0.2 | 10.7 | 10.8 | 0.1 | | |
| C ₃ A-Ort. | 0.0 | 0.5 | 0.5 | 1.2 | 1.5 | 0.3 | | |
| C ₄ AF | 9.9 | 9.8 | 0.1 | 4.4 | 4.5 | 0.1 | | |
| MgO | 3.7 | 3.6 | 0.1 | 0.7 | 0.7 | 0.1 | | |

²Each result represents the average of three replicate scans.

³Values represent mass fraction calculations from intensity measurements by profile fitting a single diffraction peak for each phase except for C₄AF, where two peaks were used.

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Appendix A

Dataplot macro file for pattern fitting and calibration using an internal standard.

| | | |
|---|-------------|---|
| dimension 40 variables | | <i>Reconfigure workspace for patterns</i> |
| skip 3 | | <i>Skip XRD header information</i> |
| . | | |
| serial read c3a_cub.sdw | c3a | <i>Read reference patterns</i> |
| serial read c3a_ort.sdw | c3ao | |
| serial read c4af.sdw | c4af | |
| serial read periclase.sdw | mgo | |
| serial read tio2ref.sdw | tio2 | |
| serial read acal101.sdw | unk | <i>Read unknown patterns</i> |
| . | | |
| ..(deleted similar commands for clarity) | | |
| . | | |
| let x = sequence 1 1 2250 | | <i>Set up two-theta scale</i> |
| let theta = 20+45*(x-1)/2250 | | |
| . | | |
| capture ASTM95.dat | | <i>Save fit data to file ASTM95.DAT</i> |
| . | | |
| fit unk c3a c4af tio2 | | <i>Fit pattern 1, with references</i> |
| . | | <i>Calculate RIR for cubic aluminate</i> |
| let RIR_CUBIC-C3A = (A1/A3)*(.1071/.58) | | |
| . | | |
| end capture | | |
| . | | |
| xlabel Degrees Two-Theta | | <i>Set up plot</i> |
| ylabel Intensity | | |
| ylimits 0 1000 | | |
| . | | |
| . | | <i>plot unknown, predicted,</i> |
| | | <i>and residual patterns</i> |
| plot unk pred resd vs. theta | | |

RM 8488 SAX QXRD - ASTM RR Calibration Constants, 88C4AF Profile
 LEAST SQUARES MULTILINEAR FIT

SAMPLE SIZE N = 2250
 NUMBER OF VARIABLES = 5
 REPLICATION STANDARD DEVIATION = 0.2355361938D+01
 REPLICATION DEGREES OF FREEDOM = 249
 NUMBER OF DISTINCT SUBSETS = 2001

| PARAMETER ESTIMATES | | | | (APPROX. ST. DEV.) | T VALUE |
|---------------------|----|------|--------------|--------------------|----------|
| 1 | A0 | | 2.06894 | (0.5156) | 4.0 |
| 2 | A1 | C3A | 0.230290 | (0.1095E-01) | 21. |
| 3 | A2 | C3AO | 0.238847 | (0.8070E-02) | 30. |
| 4 | A3 | C4AF | 1.07778 | (0.5262E-02) | 0.20E+03 |
| 5 | A4 | MGO | 0.546529E-02 | (0.5243E-02) | 1.0 |
| 6 | A5 | TIO2 | 0.423998 | (0.5834E-02) | 73. |

RESIDUAL STANDARD DEVIATION = 20.9187259674
 RESIDUAL DEGREES OF FREEDOM = 2244
 REPLICATION STANDARD DEVIATION = 2.3553619385
 REPLICATION DEGREES OF FREEDOM = 249
 LACK OF FIT F RATIO = 88.5980 = THE 100.0000% POINT OF THE
 F DISTRIBUTION WITH 1995 AND 249 DEGREES OF FREEDOM

THE COMPUTED VALUE OF THE CONSTANT MC3AC = 0.8534398E+01
 THE COMPUTED VALUE OF THE CONSTANT MC3AO = 0.1402394E+02
 THE COMPUTED VALUE OF THE CONSTANT MC4AF = 0.5992742E+02
 THE COMPUTED VALUE OF THE CONSTANT MMGO = 0.3038845E+00

THE COMPUTED VALUE OF THE CONSTANT MASS_C3A = 0.1464503E+01
 THE COMPUTED VALUE OF THE CONSTANT MASS_C3A = 0.2406508E+01
 THE COMPUTED VALUE OF THE CONSTANT MASS_C4A = 0.1028355E+02
 THE COMPUTED VALUE OF THE CONSTANT MASS_MGO = 0.5214658E-01

LEAST SQUARES MULTILINEAR FIT

REPLICATION STANDARD DEVIATION = 0.2168978453D+01
 REPLICATION DEGREES OF FREEDOM = 249
 NUMBER OF DISTINCT SUBSETS = 2001

| PARAMETER ESTIMATES | | | | (APPROX. ST. DEV.) | T VALUE |
|---------------------|----|------|--------------|--------------------|----------|
| 1 | A0 | | 1.70597 | (0.5123) | 3.3 |
| 2 | A1 | C3A | 0.228672 | (0.1088E-01) | 21. |
| 3 | A2 | C3AO | 0.239268 | (0.8018E-02) | 30. |
| 4 | A3 | C4AF | 1.06720 | (0.5228E-02) | 0.20E+03 |
| 5 | A4 | MGO | 0.493918E-02 | (0.5209E-02) | 0.95 |
| 6 | A5 | TIO2 | 0.412267 | (0.5797E-02) | 71. |

RESIDUAL STANDARD DEVIATION = 20.7836818695
 RESIDUAL DEGREES OF FREEDOM = 2244
 REPLICATION STANDARD DEVIATION = 2.1689784527
 REPLICATION DEGREES OF FREEDOM = 249
 LACK OF FIT F RATIO = 103.1548 = THE 100.0000% POINT OF THE
 F DISTRIBUTION WITH 1995 AND 249 DEGREES OF FREEDOM

THE COMPUTED VALUE OF THE CONSTANT MC3AC = 0.8715586E+01
 THE COMPUTED VALUE OF THE CONSTANT MC3AO = 0.1444840E+02
 THE COMPUTED VALUE OF THE CONSTANT MC4AF = 0.6102752E+02
 THE COMPUTED VALUE OF THE CONSTANT MMGO = 0.2824466E+00

THE COMPUTED VALUE OF THE CONSTANT MASS_C3A = 0.1495595E+01
 THE COMPUTED VALUE OF THE CONSTANT MASS_C3A = 0.2479346E+01
 THE COMPUTED VALUE OF THE CONSTANT MASS_C4A = 0.1047232E+02
 THE COMPUTED VALUE OF THE CONSTANT MASS_MGO = 0.4846784E-01